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(54) Title: BIODEGRADABLE POLYMERIC COMPOSITIONS AND PRODUCTS THEREOF

(57) Abstract.

The present invention relates to polymeric compositions that are biodegradable and that can be melt processed into various forms, including films, fibers, and nonwovens. The compositions include compatible or semi-compatible blends of biodegradable polymers and have physical and thermomechanical integrity. Films formed from preferred polymeric compositions are suitable for use as backsheets in disposable absorbent articles. In a preferred embodiment, the polymeric composition includes a polyhydroxyalkanoate and at least one other biodegradable polymer selected from aliphatic polyester-based polyurethanes, a polylactide, polycaprolactone, or a mixture of two or more of these polymers. Where the second polymer is polycaprolactone, the composition preferably also includes a third polymer for enhancing the melt processability of the composition.

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strength and/or set time of the polymer may not be suitable for good melt processing. Thus, the product tends to tear, break, or stick during processing, or the product may be unacceptably nonuniform in its physical properties. Once processed, still other properties may be needed to meet the converting, storage (including shipping and warehouse storage), or end use requirements of the polymeric product. More particularly, the product may need certain mechanical and thermomechanical properties to withstand subsequent processing and storage, and to meet end use requirements.

In addition, although several polymeric materials have been described as biodegradable, not all biodegradable materials are readily compostable. In general, for a material to be compostable, the polymeric product or large fragments thereof must undergo an initial breakup to much smaller fragments during the initial stages of a typical, commercial composting process. Otherwise, the products or large fragments may be screened out of the compost stream and may never become part of the final compost.

In commercial composting processes, the product is typically exposed to mechanical action, elevated temperatures, and/or moisture to promote the initial breakup of the product or large fragments thereof to much smaller fragments. Many biodegradable polymers exist which are sensitive to mechanical action, elevated temperatures, or moisture, such that they would individually meet the initial requirements for composting. However, few, if any, also possess the mechanical, thermomechanical, and other properties required for their practical use in a number of applications.

One practical application of biodegradable polymeric materials is in disposable absorbent articles. Although disposable absorbent articles largely comprise materials which would be expected ultimately to degrade, and although articles of this type contribute only a very small percentage of the total solid waste materials generated by consumers each year, nevertheless, there is currently a perceived need to devise such disposable products from materials which are more readily biodegradable and, preferably, which are more readily composted. There is a particular perceived need to replace polyethylene backsheet in absorbent articles with liquid impervious films of biodegradable material, since the backsheet is typically one of the largest non-biodegradable components of a

conventional disposable absorbent article.

In addition to being biodegradable, the films employed as backsheets for absorbent articles must satisfy many other performance requirements. For example, the polymer must be thermoplastic if economical, conventional, film melt processing methods, such as cast film and blown film extrusion and extrusion coating, are to be employed. Preferred materials can be melt processed into films that have substantially uniform physical properties and physical integrity. In addition, the film should have sufficient thermomechanical integrity. Thus, upon exposure to elevated temperatures, the film should maintain sufficient physical integrity to enable it to function as required at the elevated temperature, for example, to enable it to survive converting processes. In addition, even after exposure to elevated temperatures, the film should have substantial physical integrity. The film should also have certain properties to meet end use requirements. More particularly, properties such as tensile strength, tensile modulus, tear strength, impact strength, and moisture transmission rate are important since they influence the absorbent article's durability and containment while being worn.

It is an object of the present invention to provide a polymeric composition that is biodegradable and which can be melt processed to form products having substantially uniform physical properties and physical integrity. Another object is to provide such a polymeric composition that also has thermomechanical integrity. Thus, upon exposure to elevated temperatures, a product thereof should maintain sufficient physical integrity to enable it to function as required at the elevated temperature, for example, to enable it to survive converting processes. In addition, even after exposure to elevated temperatures, the product should have mechanical and other properties which enable it to be suitable for use in a number of practical applications. It is a further object of the invention to provide such a polymeric composition that can be used to form more readily compostable products. Another object of the present invention is to provide such products in the form of a fiber, nonwoven, or film. Yet another object of the present invention is to provide disposable absorbent articles such as disposable diapers, catamenials, and the like, having component parts formed from such products.

their rates of initial decomposition and breakup. Suitable blends are described herein.

Examples of high melting aliphatic polyesters include polyethylene sebacate (Melting temperature, i.e., T_m , =76°C), polyethylene succinate (5 T_m =108°C), and polyhexamethylene sebacate (T_m =78°C). Further examples can be found in the aforementioned Polymer Handbook, Third Edition Section VI, pages 56-67, previously incorporated herein by reference.

F. ELASTOMERS

10 As defined herein, a thermoplastic elastomer (alternatively referred to herein as TPE(s)) is a material that combines the processability of a thermoplastic with the functional performance and properties of a conventional thermosetting elastomer as discussed in Modern Plastics Encyclopedia, pp. 122-131 (McGraw-Hill 1990), herein incorporated by
15 reference. Commercially, there are 6 generic classes of TPE: styrenic block copolymers, polyolefin blends, elastomeric alloys, thermoplastic polyurethanes, thermoplastic copolyesters, and thermoplastic polyamides. For use in the products of the present invention, the thermoplastic elastomer must be biodegradable. From the aforementioned list of TPE
20 classes, only a select group of thermoplastic polyurethanes, specifically aliphatic polyester-based polyurethanes, are generally recognized as being biodegradable.

Biodegradable polyurethanes can be prepared from low molecular weight aliphatic polyesters derived from epsilon-caprolactone or the
25 reaction products of a diol-dicarboxylic acid condensation. In general, these low molecular weight polyesters have number average molecular weights of less than 10,000 grams per mole and frequently as low as 1,000 to 2,000 grams per mole. Examples of biodegradable polyester urethanes derived from polyethyleneglycol adipate, poly (1, 3-propanediol adipate)
30 and poly (1, 4-butanediol adipate) are disclosed in "The Prospects for Biodegradable Plastics," F. Rodriguez, *Chem Tech* (July 1971), incorporated herein by reference. Aliphatic polyester urethanes suitable for use herein are available from Morton International, Inc. under the tradename Morthane. For example, Morthane PN03-204 and Morthane

Preferred mechanically limited polymers are polylactides and cellulose esters. These polymers generally impart good melt processing to the composition, and in sufficient levels may impart high thermomechanical integrity. In addition, these materials are compatible with many polymers, with the exception of certain moisture sensitive materials as previously described. In the latter case, it has been found that the thermally sensitive polycaprolactone and polyurethane polymers can be used to compatibilize the moisture sensitive polymers and the mechanically limited polymers, as described herein.

- For improving the melt processability of the composition, generally at least about 10 weight % of the mechanically limited polymer is employed. To take advantage of the thermomechanical integrity these materials can impart to the composition, generally greater than about 30 to about 40 weight % is employed. However, when the level exceeds about 30 weight %, an additional polymer, for example, a biodegradable elastomer or polycaprolactone, or a plasticizer may be desired to offset any increase in product stiffness. This is especially true for film applications. In general, plasticizers are more efficient at reducing the stiffness than an elastomer or polycaprolactone. However, plasticizers usually also reduce the tensile strength whereas the aforementioned polymers typically increase the strength. The skilled artisan will be able to select appropriate levels of such polymers and plasticizers in light of the teachings herein to achieve a desired balance between flexibility and strength. For example, the composition may include from about 20 to about 80 weight percent of the mechanically limited polymer and from about 80 to about 20 weight percent of an elastomer, based on the total weight of the biodegradable polymers present in the composition.

- Hydrolytically cleavable polyesters are typically used in compositions containing more rapidly biodegradable polymers selected from moisture sensitive polymers, thermally sensitive polymers, polymers difficult to melt process, and mixtures thereof. Blending with such other polymers tends to enhance the initial breakup and ultimate degradation of the polyester polymers. When used, aromatic/aliphatic polyester copolymers typically make up from about 60 weight percent to about 95 weight percent of the blend, based on the total weight of the biodegradable polymers present in the composition. Oxidized ECO copolymers are useful in the compositions

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of the present invention to impart heat resistance and moisture resistance, and can be employed in amounts ranging from 1 to 99 weight percent of the total weight of the polymers in the composition. High melting aliphatic polyesters may be used in blends with other biodegradable polymers
5 wherein the high melting aliphatic polyester makes up from about 1 to about 99 weight percent of the total weight of the polymers in the composition.

When used in the compositions of the present invention, a biodegradable elastomer tends to lower the tensile modulus and to increase the ultimate elongation, tear strength, impact strength, and moisture
10 resistance relative to the composition. The elastomer is typically used in an amount of from about 10% to about 80%, preferably from about 20% to about 80%, of the total weight of the polymers in the composition. Surprisingly, it has been found that certain compositions including an aliphatic polyester-based polyurethane, which compositions are described
15 below, exhibit synergistic toughening. The tensile strength of extruded products of these compositions tends to exceed that of the individual components of the composition.

Preferred compositions of the present invention include a polyhydroxyalkanoate and one or more polymers selected from
20 polylactides, aliphatic polyester-based polyurethanes, and polycaprolactone. It has been found that such compositions tend to provide a particularly suitable combination of melt processability, mechanical properties, and thermomechanical integrity. Thus, the compositions tend to exhibit a melt strength and set time that are suitable for melt processing to
25 form products having physical integrity. The resultant products may have mechanical properties that enable their use in several applications, including backsheets and topsheets of disposable absorbent articles. The products have thermomechanical integrity as previously described.

The compositions of the present invention may thus include a
30 polyhydroxyalkanoate and at least one second polymer selected from polylactides, aliphatic polyester-based polyurethanes, and mixtures thereof. In alternative preferred embodiments, the composition includes a polyhydroxyalkanoate and polycaprolactone. According to these latter embodiments, the composition additionally includes at least one additional
35 polymer which tends to enhance the melt processability of the composition.

Any of the compositions may contain a plasticizer such as described herein, which tends to improve the mechanical properties of the composition.

In those preferred compositions which include a polyhydroxyalkanoate polymer, certain preferred conditions have been identified. For example, it has been found that at least about 10 weight % of the PHA is required to impart a sufficient level of thermomechanical integrity over the range of temperatures which may be encountered in the fabrication and storage of disposable absorbent articles. In addition, the structure of the particular PHA influences the mechanical properties and the melt processability of the composition, as previously described herein.

In those preferred compositions which include an aliphatic polyester-based polyurethane, it is generally preferred to restrict the level of polyurethane in the composition to less than about 80 weight %, based on the total weight of the polymers in the composition. At higher levels of polyurethane, films formed from the composition tend to be too soft, e.g., the tensile modulus tends to fall below about 10,000 psi. In addition, the composition tends to lack sufficient thermomechanical integrity for use in disposable absorbent articles.

Where a plasticizer is included in the preferred compositions, it has been found that at least about 5 to about 10 weight %, based on the total composition, is typically required to achieve meaningful improvements in mechanical properties. Further improvements in mechanical properties tend to occur as the plasticizer level is increased. However, at plasticizer levels greater than about 20 to about 25 weight %, processing tends to become more difficult (melt strength decreases and set time increases) and the product tends to be greasy to the touch. The plasticizer is preferably used in an amount ranging from about .5 to about 25%, more preferably from about 5 to about 20%, most preferably from about 10 to about 20%, based on the total weight of the composition.

Particular embodiments of the preferred compositions of the present invention, which include a polyhydroxyalkanoate, will now be described.

(a) Compositions including polyhydroxyalkanoate and polylactide

According to one preferred embodiment of the present invention, the

Thus, one alternative composition according to the present invention includes at least one moisture sensitive polymer, at least one thermally sensitive polymer, and at least one elastomer. In a preferred embodiment, the moisture sensitive polymer is selected from thermoplastic
5 polyvinylalcohol compositions, starch IPNs, and mixtures thereof; the thermally sensitive polymer is polycaprolactone; and the elastomer is selected from aliphatic polyester-based polyurethanes.

In another embodiment of the present invention, the composition includes at least one moisture sensitive polymer, at least one thermally
10 sensitive polymer, and at least one mechanically limited polymer. In a preferred embodiment, the moisture sensitive polymer is selected from thermoplastic polyvinylalcohol compositions, starch IPNs, and mixtures thereof; the thermally sensitive polymer is selected from polycaprolactone, aliphatic polyester-based polyurethanes, and mixtures thereof; and the
15 mechanically limited polymer is selected from cellulose esters, polylactides, and mixtures thereof.

In yet another embodiment of the present invention, the composition contains at least one thermally sensitive polymer, at least one mechanically limited polymer, and at least one elastomer. In a preferred embodiment, the
20 thermally sensitive polymer is polycaprolactone; the mechanically limited polymer is selected from cellulose esters, polylactides, and mixtures thereof; and the elastomer is selected from aliphatic polyester-based polyurethanes.

Another embodiment of the invention is a composition including at
25 least one hydrolytically cleavable aromatic/aliphatic polyester copolymer, at least one thermally sensitive polymer, and at least one moisture sensitive polymer. In a preferred embodiment, the thermally sensitive polymer is selected from polycaprolactone, aliphatic polyester-based polyurethanes, and mixtures thereof; and the moisture sensitive polymer is selected from
30 thermoplastic polyvinylalcohol compositions, starch IPNs, and mixtures thereof.

A composition of the present invention may also be formed from a blend of at least one oxidized ethylene/carbon monoxide copolymer, at least one thermally sensitive polymer, and at least one moisture sensitive

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Autovibron are found in the Imass user instruction manual titled "Automation System for Rheovibron Viscoelastometer," revised July, 1982, incorporated herein by reference. To those skilled in the use of the Autovibron or equivalent instruments, the following run conditions will be sufficient to replicate the sample failure temperature data presented hereinafter.

To measure the modulus/temperature spectrum of a film specimen, the Autovibron, is run in a temperature scan mode and equipped with an extension measuring system (EMS). A film specimen approximately 3 mm wide, 0.0254 mm thick, and of sufficient length to allow 4 to 5 cm of length between the specimen grips is mounted in the grips. The sample is selected and mounted such that the DSM is determined in the machine direction of manufacture. The apparatus is then enclosed in an environmental chamber swept with nitrogen gas. Stress is applied to the film in the length direction to achieve a deformation or strain of about 0.1 percent of the original length. A dynamic sinusoidal strain is applied to the specimen at a frequency of 110 cycles per second. The temperature is increased at a rate of 1°C per minute from room temperature to the point where the specimen melts or breaks. Temperature-dependent behavior is characterized by monitoring changes in strain and the phase difference in time between stress and strain. Storage modulus values in mega-Pascals (1 MPa ; 1.0×10^6 dynes/cm²) are calculated by the computer along with other data and displayed as functions of temperature on a video display terminal. The data are saved on computer disk and a hard copy of the storage modulus/temperature spectrum is printed for further review. The failure temperature, i.e., the temperature at which the storage modulus drops below 20 MPa, is determined directly from the spectrum.

Preferred compositions for use in fiber applications and in nonwoven, including topsheet, applications, have the following properties as determined on a 12-75 micron thick film: (a) a tensile modulus in the machine direction of manufacture of at least about 1000 MPa; and (b) a tensile strength in the machine direction of manufacture of at least about 20 MPa. These tensile properties can be determined as described above. Compositions that provide films having these tensile properties tend to provide acceptable fibers and nonwoven products. In addition, preferred compositions for use in fiber applications to be used in disposable